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TECHNICAL NOTE

No. 1375

LIMITS OF PRECISION IN THE DETERMINATION OF LATTICE

PARAMETERS AND STRESSES BY THE DEBYE-SCHERRER METHOD

By Hans Ekstein and Stanley Siegel
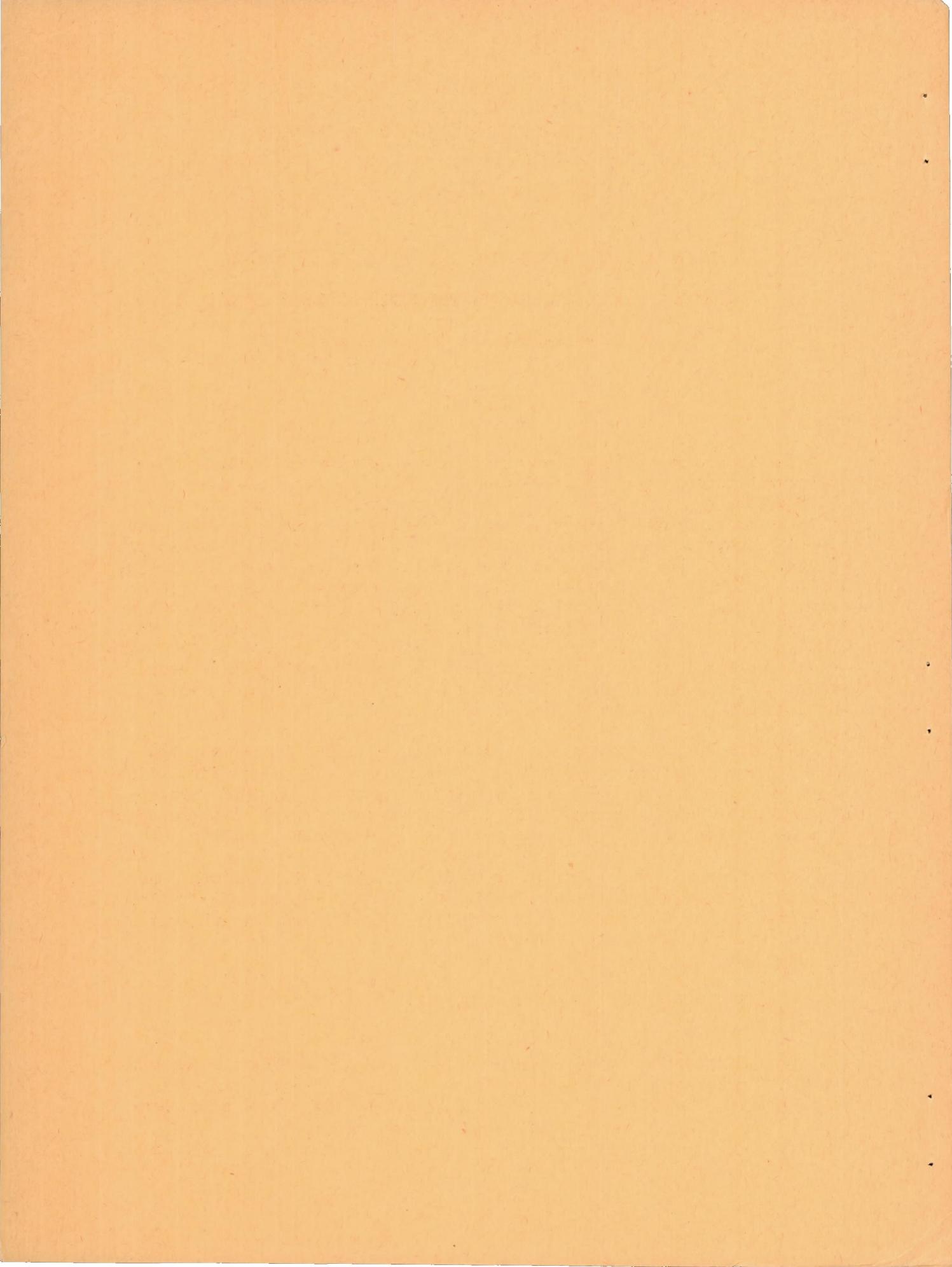Armour Research Foundation

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SUMMARY

In the accurate determination of lattice parameters by the Debye-Scherrer Method, a sharp line is desirable. It is shown that the spectral width of the characteristic radiation is the limiting factor when, by suitable experimental technique, the geometric-line width has been sufficiently reduced. This residual line width is of the order of one-quarter of the distance between the two components of the $K\alpha$ doublet. The intensity distribution in the line was calculated for the case of sufficiently large perfect crystal grains, negligible geometric width, and uniform angular distribution of crystal grains. As the tube and object are usually immobile in stress measurements, the case of uniform distribution is only approximated when the crystal-grain size is sufficiently small. Otherwise, the actual intensity distribution is a jagged curve, which makes accurate measurements impossible.

Experiments were performed with copper radiation on zinc samples. The Bragg angle in this case was 87.53° so that the geometric-line width could be made small in comparison with the spectral-line width. Photographs taken with samples of different crystal-grain sizes show the transition from the jagged to the theoretical, smooth intensity curve.

Even when the crystal-grain orientation is perfectly uniform, the recording of the intensity distribution will entail errors. Errors due to irregular fluctuations of film density are determined for subjective and objective measurements of the line center.

INTRODUCTION

In attempting to improve the precision of X-ray diffraction measurements, the first difficulties were due to the two obvious facts which distinguish X-rays from optical rays: namely, that no lenses exist for

X-rays and that there is some penetration of X-rays into the specimen so
that the location of the object is somewhat indeterminate. Limitations
of accuracy by these facts, which will be called the geometrical factors,
have been discussed thoroughly in the literature, and great progress in
improved apparatus and calculating methods has been made in order to over-
come these limitations. (See references 1 to 4.) To the extent to which
the refinements eliminate errors of a geometrical nature, other sources of
error, hardly discussed thus far, become important. The following discus-
sion treats what seems to be the next obstacle to be overcome in the grad-
ual improvement of accuracy, with particular emphasis on the application
of lattice distance measurements to stress determinations.

One source of error is found in the physical nature of the specimen.
If the crystal grains are not perfectly periodical arrays of atoms, the
accuracy of measurement is limited by the amount of periodicity. Too
small grain size is known to broaden lines, thereby reducing the sharpness
of the diffraction lines. Finally, even if each crystal grain may be con-
sidered perfect, the strain in a polycrystalline sample under stress will
be nonhomogeneous so that a whole range of lattice parameters will be ob-
served in any single measurement. In this report, all errors of this na-
ture will be disregarded and attention will be centered upon the errors
inherent in the measuring method itself. Thus it will be assumed for
this purpose that all individual crystal grains are perfect; that is, of
sufficient size, perfectly periodic, and of identical structure.

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sponsored by and conducted with the financial assistance of the National
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THEORETICAL CONSIDERATIONS

For accurate measurement of the line position, a sharp line is desir-
able. Disregarding the geometrical factors, the narrowness of the dif-
fraction line is limited by the spectral impurity of the primary charac-
teristic radiation. Although in most experiments the width is determined
by the geometrical factors, the lines with glancing angles close to 90°
owe their width predominantly to the spectral impurity, when the geometri-
cal factors are as favorable as is presently feasible as will be shown in
the following discussion. But it is precisely this region of back reflection
where the line position is most sensitive to small changes of lattice param-
eters. It becomes necessary therefore to investigate this spectral width.

Suppose that a randomly distributed mass of perfect crystals is used
and that the divergence, beam width, and depth of penetration are negligi-
ble. A Debye-Scherrer line would have a width corresponding to the range
of wavelengths in the primary beam.

To each wave length λ, there corresponds on the X-ray photograph an
angle $\phi = 2\theta$ given by

$$\lambda = 2d \sin \phi/2 \tag{1}$$

where the order number n is considered to be included in the effective
lattice spacing d. The intensity of a spectral line is given by

$$I(\lambda) = \frac{A}{(\lambda - \lambda_0)^2 + \left(\frac{w}{2}\right)^2} \tag{2}$$

where λ_0 is the wavelength corresponding to the maximum intensity,
w is the width of the line (fig. 1), and A is a constant.

Now, define an angle $\phi_0/2$ so that

$$\lambda_0 = 2d \sin \phi_0/2 \tag{3}$$

By use of equations (1) to (3) and substitution into equation (2),
there is obtained for the intensity diffracted by all crystals

$$I'(\phi) = \frac{F(\phi)}{(2d)^2 (\sin \phi/2 - \sin \phi_0/2)^2 + \left(\frac{w}{2}\right)^2} \tag{4}$$

where the function $F(\phi)$ depends on the intensity of the primary beam and
the number of crystals which are oriented so as to reflect at a definite
angle ϕ if excited by the proper wavelength.

Dividing through by $(2d)^2$ and using equation (3) yields

$$I'(\phi) = \frac{B'(\phi)}{(\sin \phi/2 - \sin \phi_0/2)^2 + \left(\frac{w}{2} \frac{\sin \phi_0/2}{\lambda_0}\right)^2} \tag{5}$$

If ϕ is not too close to 180° and the line is not too broad, there
can be substituted

$$\sin \phi/2 - \sin \phi_0/2 = \Delta\phi/2 \cos \phi_0/2 \tag{6}$$

Thereby equation (5) becomes

$$I'(\phi) = \frac{B(\phi)}{(\Delta\phi)^2 + \left(\frac{w}{\lambda_0} \tan \phi_0/2\right)^2} \tag{7}$$

where $B(\phi)$ is again a function of the crystal distribution.

The function $B(\phi)$ expresses the accidental orientation of crystal grains with respect to the primary beam. As the function is of statistical nature and entirely unknown in every particular case, a measured intensity distribution $I'(\phi)$ cannot be used to determine the angle ϕ_0, and thereby the lattice parameter d. In ordinary lattice-constant measurements, this difficulty is usually overcome by rotating or oscillating the sample about an axis normal to the primary beam, thereby causing the crystal grains to assume successively an infinite number of orientations with respect to the beam. In this way, the statistical function $B(\phi)$ is "averaged out" so that it becomes practically a constant over the diffraction line. The particular difficulty of stress measurements is that, for obvious mechanical reasons, it is usually impossible to rotate the specimen or - which has the same effect - oscillate the X-ray tube. It is possible, however, to obtain some smoothing of the erratic distribution function by rotating the recording film about the primary beam as an axis, and this is the usual procedure. Nevertheless, it is not easy to obtain smooth intensity distributions in this way. It is shown in the section on Experimental Work that the line will have a smooth intensity distribution only under particularly favorable circumstances. Otherwise, high resolution of details, which is necessary for extreme precision measurements, exhibits the erratic structure of the line. If nonphotographic means of intensity measurement are used; that is, ionization chambers or Geiger-Mueller counters, the situation is even worse, because the smoothing effect of the rotation cannot be used.

One limitation of the accuracy of stress measurements is thus given by the statistics of crystal-grain orientation. If the number of crystals "viewed" by the primary beam is small, the function $B(\phi)$ will be erratic.

The ideal case occurs when the crystal orientation is statistically uniform; that is, practically, when a very large number of crystals contribute to the formation of the diffraction line. In this case $B(\phi)$ and $B'(\phi)$ are practically constant over the line width, and equations (5) and (7) become

$$I(\phi) = \frac{B'}{(\sin \phi/2 - \sin \phi_0/2)^2 + \left(\frac{w}{2} \frac{\sin \phi_0}{\lambda_0}\right)^2} \qquad (5a)$$

and

$$I(\phi) = \frac{B}{(\Delta\phi)^2 + \left(\frac{w}{\lambda_0} \tan \phi_0/2\right)^2} \qquad (7a)$$

where B and B' are now constants. This case of "perfect statistics" will be considered in the following discussion.

Comparison between equations (7a) and (2) shows that the form of the Debye–Scherrer line is the same as that of the spectral line and that

$$W = \frac{2w}{\lambda_0} \tan\left(\frac{\phi_0}{2}\right) \tag{8}$$

is the angular width of the Debye–Scherrer line. Equation (8) expresses the well-known fact that the dispersion increases proportionally with $\tan \theta$.

If the intensity curve given by equation (7a) could be recorded in a perfectly exact manner, the position of the maximum intensity ϕ_0 could be determined with any degree of precision, and the lattice spacing could be calculated by equation (3). Actually, the granular structure of the photographic film makes the recorded intensity curve deviate from the form of equation (7a). Further errors are of subjective nature if the evaluation is visual or are due to the amplifier or curve-tracing mechanism if a microphotometer is used.

Similar sources of error appear when ionization chambers or Geiger–Mueller counters are used with very narrow slits. Even then, these instruments will hardly be used for high-precision measurements of this nature, because of their inability to average crystal positions by rotation. The determination of ϕ_0 will therefore be possible only within a finite error $\delta\phi_0$.

Let

$$r = \frac{\delta\phi_0}{W} \tag{9}$$

be the relative error of the measurement of the maximum of a curve with width W. By logarithmic differentiation of equation (3),

$$0 = \frac{\delta d}{d} + \delta(\phi_0/2) \cot(\phi_0/2) \tag{10}$$

For the absolute magnitude of the relative error $\left|\frac{\delta d}{d}\right|$ of the lattice spacing, there is obtained

$$\left|\frac{\delta d}{d}\right| = \left|\delta(\phi_0/2) \cot(\phi_0/2)\right| \tag{10a}$$

which with equations (9) and (8) gives

$$\frac{\delta d}{d} = r \frac{w}{\lambda_o}$$ (11)

According to Compton and Allison (reference 5), the widths of two representative X-ray lines are as follows:

	λ_o(XU)	w(XU)	w/λ_o
Cu Ka_1	1537.4	0.58	3.7×10^{-4}
Co Ka_2	1789.2	.95	5.3×10^{-4}

and the order of magnitude of w/λ_o is the same for most X-ray lines. Thus, the relative error in lattice spacing is roughly

$$\frac{\delta d}{d} = 4 \times 10^{-4} \ r$$ (12)

What accuracy then may be expected for a photographic determination of d? Most measurements reported in the literature were made by visual evaluation. Subjective as well as objective evaluations of the precision reported in the section on Experimental Work have shown that it is possible to determine the position of maximum intensity with an uncertainty of 1/10 to 1/30 the line width. This value is subject to some variation dependent upon the angle of diffraction and the film-to-specimen distance.

If

$$r = \frac{1}{12} \quad \text{for steel}$$

$$r = \frac{1}{30} \quad \text{for zinc}$$

are assumed in accordance with the section on Experimental Work, equation (12) leads to a relative error

$$\frac{\delta d}{d} = 3.3 \times 10^{-5} \quad \text{for steel}$$

$$\frac{\delta d}{d} = 1.3 \times 10^{-5} \quad \text{for zinc}$$

In fact, the highest accuracy claimed in the literature is about $\frac{\delta d}{d} = 2 \times 10^{-5}$. Inasmuch as no geometrical and statistical errors were considered, this claim would seem optimistic. The experimental measurements, however, use several lines and several separate pictures, so that

the relative error may be slightly decreased by the number of measurements.

It is concluded that the claimed accuracy of $\frac{\delta d}{d}$ = 2 × 10   seems
optimistic, but just possible if all errors, except those due to the
photographic film, are disregarded. The comparison between the error due
solely to spectral-line width (in connection with film grain), on the one
hand, and the error reported in the literature, on the other hand, shows
that the <u>limit in eliminating error sources other than the spectral-line
width has already been reached.</u> This justifies the failure to discuss
error sources of geometric nature. It is somewhat surprising that the
spectral-line width turns out to be the limiting factor for an increase
of accuracy, for most papers on the subject treat only the geometric
factors.

In order to use the preceding results to make any inferences as to
the limits of accuracy of stress measurements, the ideal case must be
considered where the stressed crystal grains would still remain perfect
diffractors, where the geometric conditions are perfect, and where the
statistical distribution is uniform. Under these conditions, the limit
of accuracy is given by the uncertainty of the photographic determination
of the maximum intensity of the Debye-Scherrer lines.

For a picture taken by back reflection from the sample surface, the
sum of the principal stresses $\sigma_1 + \sigma_2$ in the plane of the surface is
given by

$$\sigma_B = \sigma_1 + \sigma_2 = \frac{E}{\nu}\frac{\Delta d}{d} \tag{13a}$$

where E is Young's modulus, ν Poisson's ratio, and Δd the change of
lattice spacing due to stress. For almost grazing incidence,

$$\sigma_G = E \frac{\Delta d}{d} \tag{13b}$$

The error of stress measurement due to an error $\delta(\Delta d)$, or which is the
same, $\sqrt{2}\delta d$ (reference 6), is then

$$\delta\sigma_B = \frac{E}{\nu}\frac{\delta d}{d}\sqrt{2} \tag{14a}$$

and

$$\delta\sigma_G = E \frac{\delta d}{d}\sqrt{2} \tag{14b}$$

for back and grazing incidence, respectively.

By use of equation (12), there is obtained

$$\delta\sigma_B = \frac{E}{\nu} r \, 4 \times 10^{-4} \sqrt{2} \qquad (15a)$$

and

$$\delta\sigma_G = E r \, 4 \times 10^{-4} \sqrt{2} \qquad (15b)$$

respectively.

The values of E and ν for steel and zinc are listed as representative examples:

	Poisson's ratio, ν	Young's modulus, E (psi)
Steel	0.3	28×10^6
Zinc	.3	13×10^6

With these values, the stress error becomes

$$\delta\sigma_B = \begin{cases} 52,600 \text{ r psi} & \text{for steel} \\ 24,400 \text{ r psi} & \text{for zinc} \end{cases} \qquad (16a)$$

for back reflection and

$$\delta\sigma_G = \begin{cases} 15,800 \text{ r psi} & \text{for steel} \\ 7,320 \text{ r psi} & \text{for zinc} \end{cases} \qquad (16b)$$

for almost grazing incidence.

Grazing incidence should be eliminated for accurate measurements because the beam impinges on too large a portion and focusing is impossible. Choose for typical experimental arrangements, cobalt radiation for steel, copper radiation for zinc, and a 5-centimeter film-to-specimen distance. From the measurements reported in the section on Experimental Work and by using $r = \frac{1}{30}$ for zinc and, by interpolation, $r = \frac{1}{12}$ for steel, there is obtained

$$\delta\sigma_B = \begin{cases} 4380 \text{ psi} & \text{for steel} \\ 810 \text{ psi} & \text{for zinc} \end{cases} \qquad (17a)$$

These accuracies coincide with the accuracy reported in most publications. Occasionally, accuracies as high as 2000 psi are claimed for steel, but, in view of all assumptions made in arriving at equation (17a), such claims seem hardly reasonable.[1]

The difficulties of improving the accuracy are illustrated in figure 2. This figure shows the two intensity distribution curves for the unstressed and stressed (2800 psi) steel with a film-to-specimen distance of 5 centimeters. The curves are calculated according to equation (5a), that is, for ideal geometry and ideally uniform crystal orientation. If nothing but the finite grain size of the film is added, it becomes apparent that a visual or photometric differentiation between the two curves of figure 2 is hardly possible.

It is concluded that the limit of accuracy is given essentially by the spectral-line width and the uncertainty of determination of the center of the Debye-Scherrer line. With respect to geometric factors, the limit evidently has already been reached, or in other words, remaining geometrical errors are already reduced, in the present technique, to at least the same order of magnitude as the error due to the spectral-line width.

EXPERIMENTAL WORK

According to equation (12), the relative uncertainty in the lattice spacing is approximately 4×10^{-4} r, where r is the uncertainty of measurement of the diffraction-line center. The accuracy with which r can be determined will depend on two factors, the statistical arrangement of the crystal grains in the sample and the quality of the film.

Uncertainty of Measurement Due to the Statistical Fluctuations

of Crystal Orientation

A study of the effects of the sample statistics on the diffraction line requires:

1. A Debye-Scherrer line wide in comparison with the geometrical width so that the geometrical factors are negligible

2. A line wide in comparison with the film grain size so that irregularities of the film density may be disregarded

3. Large crystallites and nearly perfect

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[1]It is true that a somewhat stringent definition is used here for the "error," namely, three times the standard deviation; whereas other authors may mean the standard deviation.

In order to meet requirements 1 and 2, high dispersion is necessary; that is, a Bragg angle θ near $90°$ is required, which calls for an unusual combination of wavelength and lattice parameter. A study of a number of metals showed that zinc will produce a reflection at $87.53°$ with Cu Kα_1 radiation. With lattice constants $a_0 = 2.6595$ A and $c_0 = 4.9368$ A, for a 213 plane, is obtained

$$d = 0.76950 \text{ A}$$

This plane gives a reasonably strong reflection. The choice of zinc is fortunate, too, in that its annealing temperature is quite low and large, perfect crystal grains may be easily produced. Condition 3 may thus be fulfilled with little difficulty.

The geometry of the film and collimator system must be so chosen that conditions 1 and 2 are fulfilled. According to equation (8), the width W of the Debye-Scherrer line at the Bragg angle $\phi_0/2$, and for the wavelength λ_0, is given by

$$W = 2 \frac{w}{\lambda_0} \tan \phi_0/2$$

With the following constants,

$$w = 0.00058 \times 10^{-8} \text{ centimeter}$$

$$\lambda_0 = 1.5374 \times 10^{-8} \text{ centimeter}$$

$$\phi_0/2 = 87.53°$$

there is obtained

$$W = 0.0174 \text{ radian}$$

This spectral width should be several times larger than the geometrical width so that the effects of the geometrical width will be negligible.

With collimating pinholes 0.051 centimeter in diameter and spaced 7.62 centimeters, the maximum angular divergence of the incident beam is 0.013 radian. In the conventional back-reflection technique used in these experiments, the emergent pinhole collimator is almost at the surface of the film, and the effective beam source is 3.8 centimeters in back of the film. Thus, by increasing the distance between the film and specimen, a geometrical focusing condition is more nearly realized. On the other hand, the width of the line on the film, caused by the spectral

dispersion, will increase as the film-to-specimen distance increases.
Thus, if a film-to-specimen distance of 15 centimeters is chosen, the
spectral width of the line on the film is 2.64 millimeters; whereas the
geometrical width of the line is approximately 0.5 millimeter. The spec-
tral width is, accordingly, about five times that of the geometrical
width and conditions 1 and 2 are fulfilled.

Experimental technique.- The X-ray unit is a commercial type with a
voltage range of 30 to 50 kilovolts and a corresponding tube current
range of 25 to 16 milliamperes. The back-reflection camera is of a con-
ventional type with the film cassette mounted normal to a shaft contain-
ing the collimator system. The shaft may be rotated by a small motor.
The cassette is designed to accommodate reflections up to 89° using a
film-to-specimen distance of 15 centimeters. The sample holder is so
designed that the sample may be rotated in a plane normal to the beam.
Radiation filtered with nickel foil is used throughout the experiments.

According to equation (7a) a diffraction line is expected to be
smooth and continuous only if the number and the statistical distribution
of the crystal grains are correct. In order to observe the influence of
grain size upon the smoothness of the diffraction line, three samples
were prepared in the following manner:

Sample A.- A rod of very pure zinc exhibiting large crystals was
filed in order to prepare a flat surface. The surface was left in this
condition and photographed.

Sample B.- A piece of flat cold-rolled zinc was polished, annealed,
and etched.

Sample C.- Annealed zinc dust was separated into a fraction of small
uniform particles.

Diffraction lines with Bragg angles of the order of 65° to 69° were
chosen as reference lines from which the film-to-specimen distance D
could be calculated. This choice is justified because these lines are
not too sensitive to structural changes, and the D value so obtained is
good enough for comparative purposes.

Discussion of photographs.- A diffraction pattern of sample A is
shown in figure 3. The exposure time is 6 hours and only the film has
been rotated. The 213 reflection shows considerable structure, being
composed of many sharp maximums. Figure 4 is a diffraction pattern of
sample B; the exposure time is 5 hours and only the film has been rotated.
Subsequent diffraction patterns of various regions of samples A and B
show a variety of line structures; one to five sharp maximums and many
weak maximums may be superimposed upon an apparently continuous back-
ground.

In order to improve the statistics, the sample must be rotated about
an axis normal to the beam. In general, for stress measurements, this is
not feasible because of mechanical reasons. However, if an attempt is
made to "average" the reflection by rotating, say, sample B about its axis
coincident with the X-ray beam, figure 5 results. In this figure the film-
to-specimen distance has been reduced to 10 centimeters. The line is
made up of concentric swirls caused by large grains rotating in the beam
and reflecting over a small angular range of rotation. If the sample is
rotated off-center so that different regions of the sample are in a posi-
tion to diffract, the line shows a crosspatch of structure.

If the specimen is to remain stationary, a smooth continuous diffrac-
tion line will be obtained only if the number and orientation of the
crystal grains are correct. Sample C was prepared for that reason. Zinc
dust was mixed with bromoform and a fine uniform fraction was allowed to
settle on a plate. A 6-hour photograph obtained by rotating the film
only is shown in figure 6. Generally, the line is quite uniform although
a slight amount of structure is observed.

The intensity distributions of the diffraction patterns shown in
figures 7, 8, and 9 were prepared from microphotometer tracings of fig-
ures 3, 4, and 6, respectively. The experimental curves are compared
with the curve obtained from equation (5a) that is valid for uniform dis-
tribution. Although sample C showed slight structure near one edge of
the line, this structure has been disregarded in producing figure 9. The
experimental and theoretical curves are not given on an absolute scale
but have been matched by adjusting one point on the intensity scale for
each experimental curve. The agreement between the experimental and the-
oretical curves of figure 9 (very small grains) is quite good and the
asymmetry of the diffraction line is very apparent. Thus, when the crys-
tal grains are large, the fluctuation of the angular distribution of
crystals is so large that $B(\phi)$ cannot be considered a constant; rather
$B(\phi)$ will be irregularly jagged.

Uncertainty of Measurement Due to the Photographic Film

It has been shown that the diffraction line necessarily has a mini-
mum width. The question is: How accurately can the center of this line
be measured if all other conditions are perfect?

Although the usual measurements of this type are visual, the uncer-
tainties of subjective evaluations have already led some authors to ob-
jective measurements. (See reference 7.) The precision of both methods
is discussed in the following sections. The standard deviation σ is deter-
mined in both methods. In a normal distribution of errors, the frequency of
errors outside the range $\pm 3\sigma$ is very small; the number of observations
beyond this limit will be only less than 1 percent of the total number of

observations. Hence, with the expectation that practically all measurements of the line center will fall within the range $\pm 3\sigma$, the relative uncertainty of the line measurement becomes

$$r = \frac{3\sigma}{W}$$

Subjective Precision.— A sharp and a broad line, both obtained by rotation of the sample, were chosen for this measurement. The center of each line was measured by four observers using a comparator with cross hairs. Each line was magnified sufficiently to be suitably convenient for all observers. The data of each observer were averaged. From these average values a new average was determined from which the standard deviation was calculated. The results may be tabulated as follows:

Table I

	$D\sigma$ (cm)	DW (cm)	r
Sharp line	0.00075	0.015	1/7
Broad line	.00074	.077	1/35

where D is the distance between the film and specimen. Obviously, the number of measurements is so small that no exaggerated weight should be attached to these numbers. Furthermore, the film quality, time of exposure, and film-development conditions may change these results. Nevertheless, the increased accuracy for broader lines seems to be a fact.

This is also in agreement with what would be expected theoretically. Indeed, if the line width is of the order of one grain or cluster of grains, the ratio r will be of the order 1. If, on the other hand, the line width is very large in comparison with the "quasi period" of the fluctuations of density, the uncertainty of the maximum will be relatively small so that r should decrease.

Interpolation between the two values given in table I for the case of the 310 reflection of iron by $Co K\alpha_1$ radiation, using the usual film-to-specimen distance of 5 centimeters, gives

$$r = \frac{1}{12}$$

which may be taken as a representative value for the subjective accuracy
if all reservations previously made are remembered.

Objective precision.- The objective studies were performed by deter-
mining the median of the microphotometer tracing of a line. In observing
the film, the field of view will show grain clusters, film defects,
scratches, dust, and so forth. The eye automatically decides which of
these are spurious and mentally subtracts them from the field of view.
A limit of accuracy is reached, however, because the eye is unable to dis-
tinguish between two regions of the film which are slightly different in
density. On the other hand, the microphotometer will record any spurious
fluctuations of density which the eye disregarded, but for broad lines
these fluctuations will be averaged out. Therefore, the objective method
may be expected to be superior for wide lines. For this reason, broader
lines were chosen to be evaluated by the microphotometer.

A fine capillary of glass was filled with zinc dust and rotated in
the X-ray beam so that perfect statistics would be guaranteed. The 213
reflection was recorded on films of different grain size, one coarse and
the other finer grained. A sharper line was also recorded on the coarse-
grained film.[2] For a film-to-specimen distance of 10 centimeters, the
coarse film required an exposure time of $4\frac{1}{2}$ hours; whereas the finer film
required 18 hours.

Microphotometer tracings were obtained by scanning along the radius
of the diffraction line. A number of tracings of each line was obtained
by slightly rotating the film in the microphotometer and scanning along
a new radius. The microphotometer beam had a width of 0.01 millimeter
and a length of 1 millimeter. Two microphotometer tracings were produced
for each setting of the film. Five sets, or a total of 10 tracings, were
so obtained for each film. The reason for producing two tracings per film
setting is to allow two observers to make measurements on the same curve
and thus reduce subjective factors.

Typical tracings are given in figures 10 to 12. Figure 10 is the
broad line on coarse-grained film, figure 11 the broad line on finer-
grained film, and figure 12 the sharp line on coarse-grained film. These
microphotometer tracings were produced at high magnification in order to
reduce measurement errors. The X coordinates given in these figures
simply represent distances along the tracings. Since the diffraction line
is asymmetrical, it was more convenient to measure the median by weighing,
than to determine the X-coordinate of the centroid.

Each film carried a fiducial mark which served as the reference
point from which the median could be determined. Distances were measured

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[2]   Obviously, no line exhibiting an overlapping $K\alpha$ doublet could be
used.

along the tracing from the fiducial mark to regions on either side of the
maximums where the density dropped to a low value and became constant.
These distances were constant for each film and served as the boundaries
on either side of the maximums. The curves were then cut out between the
boundaries and cut in half. Subsequent cuts were made until a chemical
balance showed the two halves to be of equal weight (or area). After a
balance had been effected, the curve from which material had been cut was
placed back in position in the tracing sheet from which it had been re-
moved. The distance between the fiducial mark and the edge of the cut
curve was measured. This value is the X coordinate of the median.

Each observer determined the median of the same tracing. The two
values were averaged. A new average was then obtained for all tracings
of the particular film, and the standard deviation σ was then deter-
mined from this value. Again 3σ was taken as the value beyond which
the number of observations having this error would be negligible. The
results are given in the following table:

Table II

	$D\sigma$ (cm)	DW (cm)	r
Coarse film, sharp line	0.00180	0.034	1/6
Fine film, broad line	.00259	.176	1/23
Coarse film, broad line	.00336	.172	1/18

The general tendency toward increased accuracy for wider lines is
again apparent. However, it is surprising that for lines broader than
those evaluated visually, the accuracy is lower. It seems that the dis-
criminating ability of the eye makes it superior to the microphotometer
for the usual range of line width. This explains the reluctance of most
observers to use objective methods.

A more accurate method of objective evaluation would first have com-
pleted, by the method of least squares, the best fitting smooth curve
corresponding to each microphotometer tracing and would then have deter-
mined the median. However, this procedure seems too cumbersome for rou-
tine use.

It is doubtful whether the present choice of exposure time and back-
ground density are the most favorable. It is known (reference 8) that the
fluctuation of density decreases as the density increases. This suggests
that an exposure to a uniform beam prior to the diffraction exposure might
improve the accuracy. However, this would tend to make the density curve
flatter, so that the gain in smoothness might be offset by the loss of
sharpness. Only further investigations can answer the question.

CONCLUSIONS

From an investigation of the limits of precision in the determination of lattice parameters and stresses, the following conclusions were made:

The sharpness of the diffraction line is limited by the spectral breadth of the primary characteristic radiation. Under conditions where a large number of perfect crystals are randomly oriented, the diffraction line will be perfectly smooth and uniform. If the sample statistics are poor and the diffraction line cannot be smoothed by proper rotation of the specimen (as in most stress measurements), the diffraction line will exhibit an irregular intensity distribution. This makes a precise determination of the intensity maximum, and, thereby, of the lattice parameter, impossible.

Even when the statistical fluctuations of grain orientation are eliminated, the accuracy is limited by the imperfection of the photographic film, which entails erratic irregularities of the photographic density distribution.

Objective and subjective evaluations of the center of a photographically recorded line lead to uncertainties in lattice spacing d. The relative error $\delta d/d$ in determining the lattice spacing is approximately 2×10^{-5} as an order of magnitude. This value determines the accuracy with which stress measurements may be made.

Armour Research Foundation,
      Chicago, Ill., June 11, 1947.

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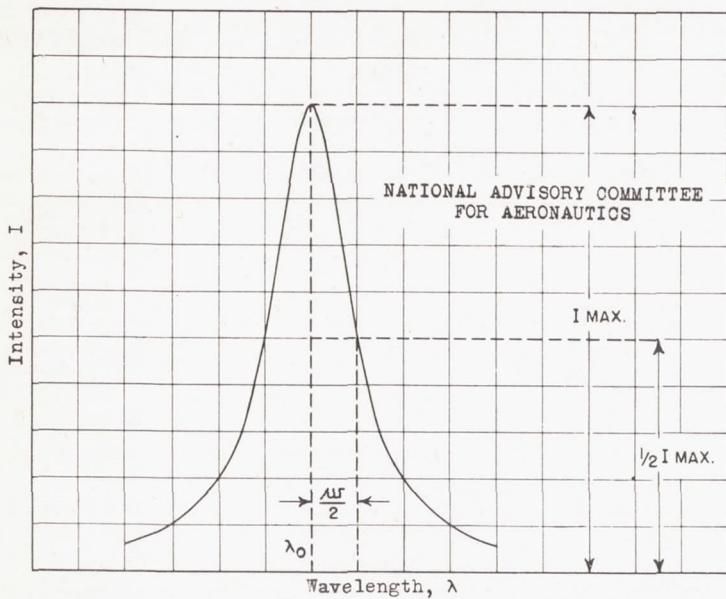
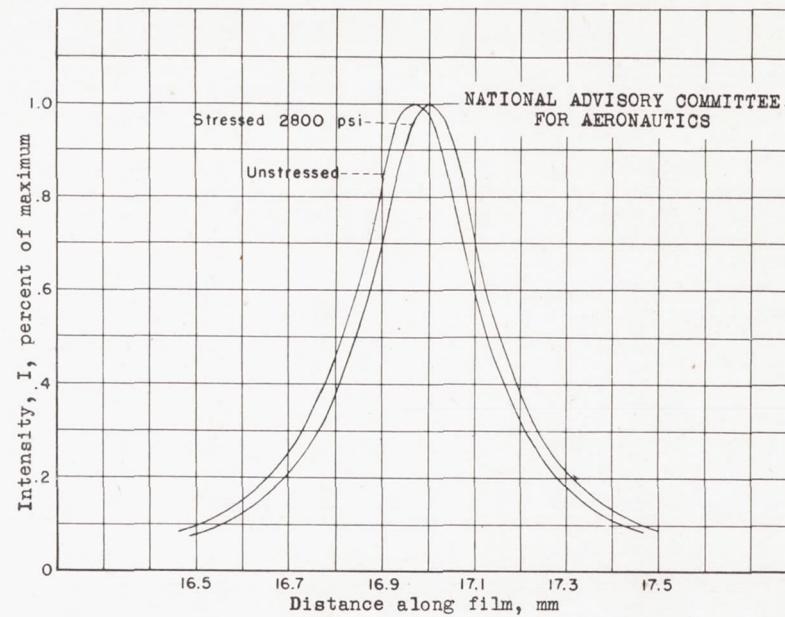Figure 1.- Intensity of spectral line as function of wave-
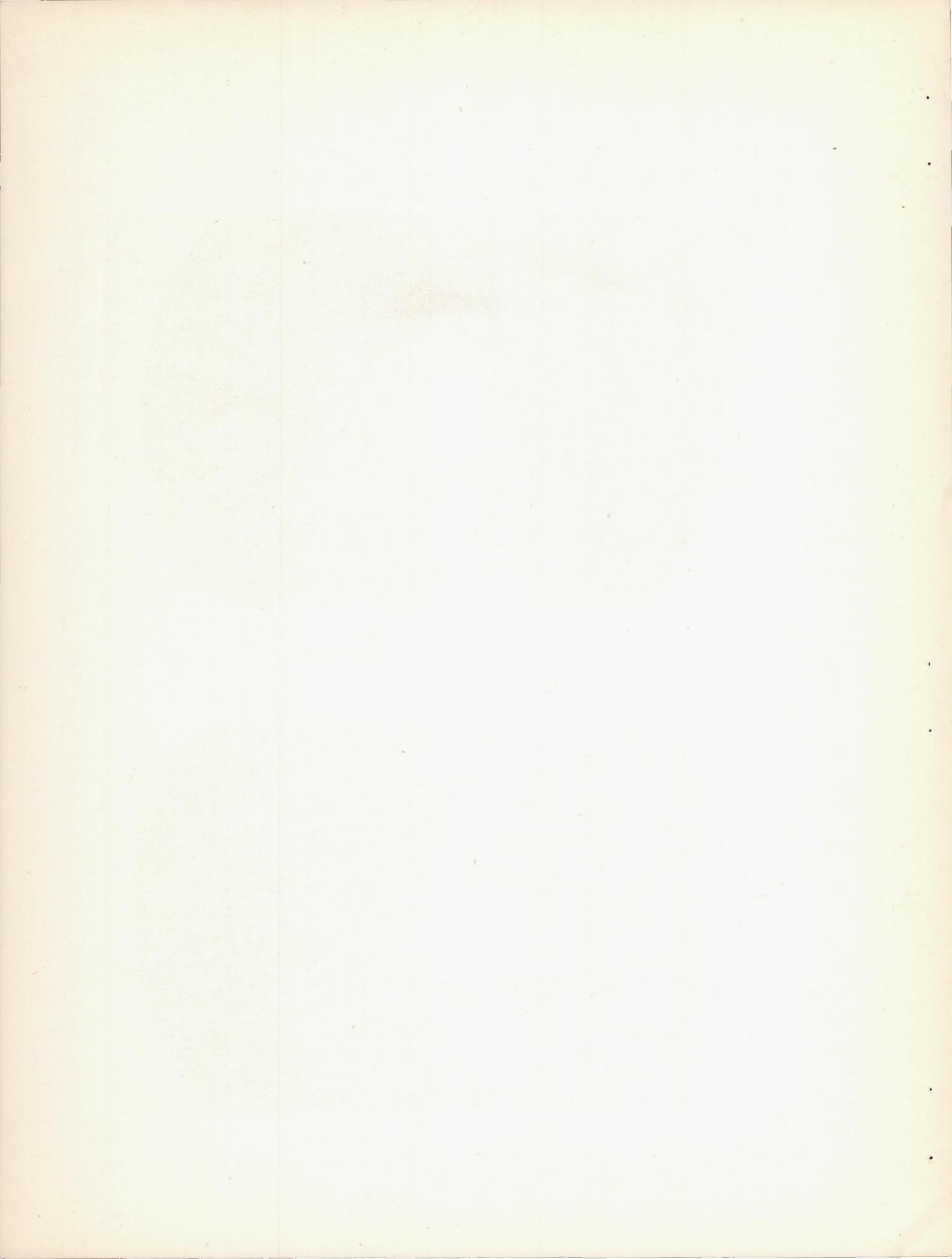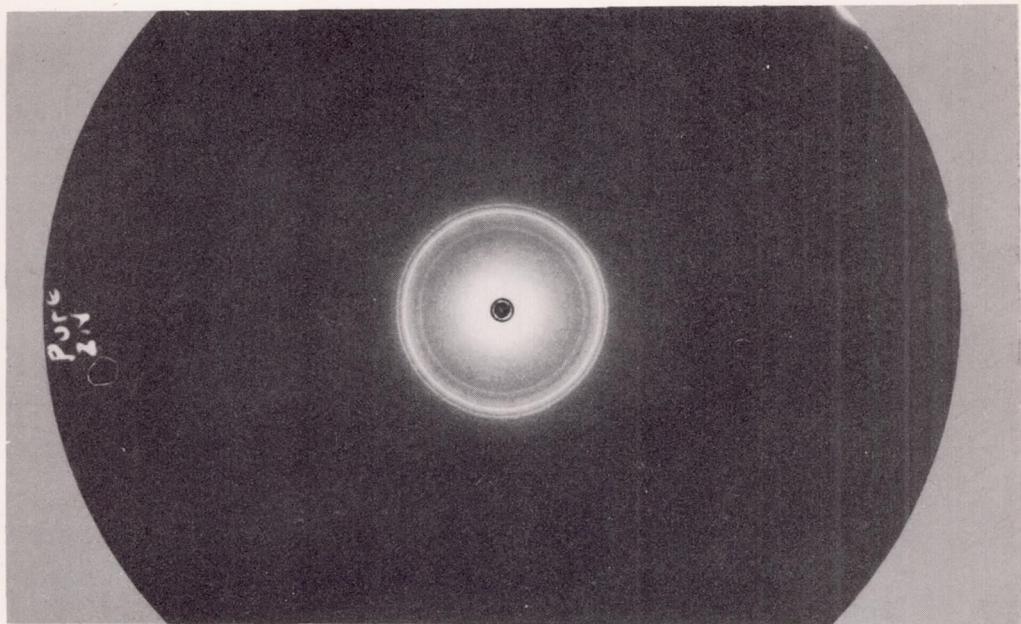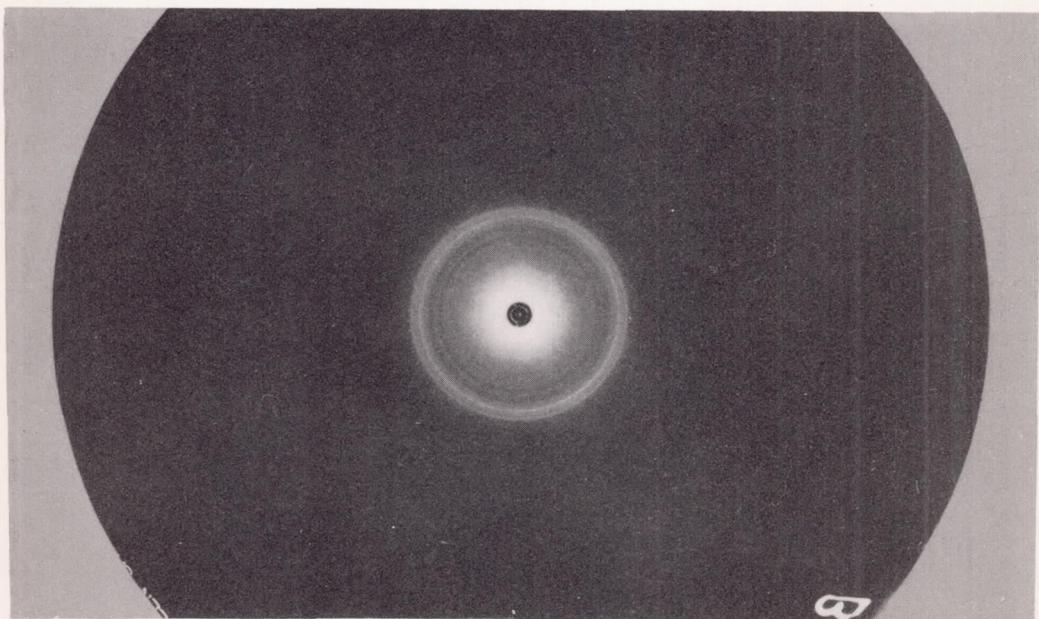length.

Figure 2.- Intensity distribution for stressed and unstressed
steel. Film-to-specimen distance, 5 centimeters.

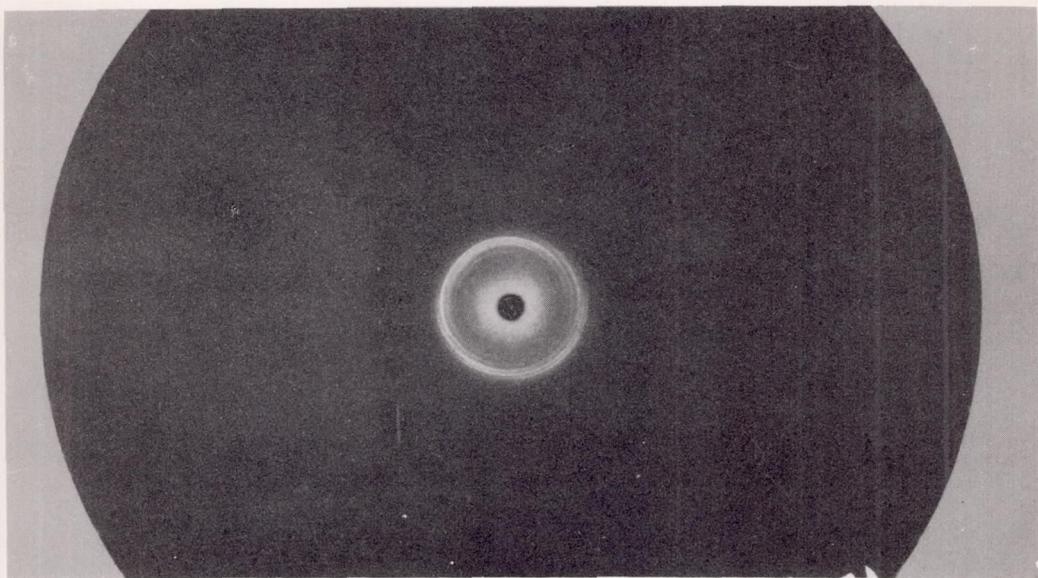Figure 3.- Diffraction pattern of sample A. Exposure time, 6 hours; film rotated.

Figure 4.- Diffraction pattern of sample B. Exposure time, 5 hours; film rotated.

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Figure 5.- Diffraction pattern with sample B rotated.

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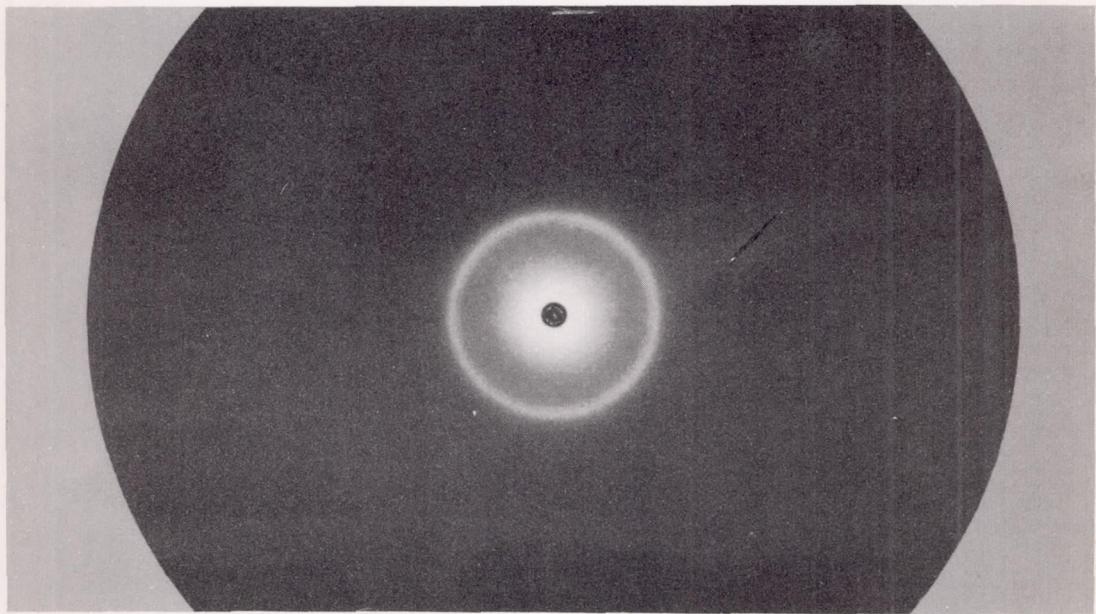Figure 6.- Diffraction pattern of sample C. Exposure time, 6 hours; film rotated.